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Glycerol-enriched heterogeneous catalyst for biodiesel production from soybean oil and waste frying oil

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Abstract

In the present work, biodiesel production using a glycerol enriched heterogeneous catalyst was studied. For that purpose, the catalyst performance at different glycerol concentrations and reaction conditions (under ambient atmosphere) was evaluated and two triglyceride sources were used. The most active catalyst was produced using CaO, glycerol and methanol at a mass ratio of 1:1.6:13.4, respectively. By per- forming the transesterification reaction under ambient atmosphere during 2 h at 333 K, using 0.4 wt.% of catalyst and 7:1 methanol to oil molar ratio, a good quality product was obtained (EN 14214) using both soybean oil and waste frying oil. The catalyst could be re-used during four cycles and could also be pre- pared by using ethanol instead of methanol (with differences <4% on product conversion). The glycerol by-product, being rich in calcium soaps, might additionally be used for the enrichment of animal diets. The present process allowed the production of biodiesel from different triglyceride sources using a very active heterogeneous catalyst at competitive reaction conditions compared to the homogeneous process and also enabled a two-way recycling of the glycerol by-product.

1. Introduction

Biodiesel is a biofuel that can be used to replace fossil diesel, presenting several environmental, economic and social advantages, thoroughly described [1]. Biodiesel might be produced from different triglycerides sources such as vegetable oils (that can be edible, non-edible or waste oils), animal fats (mostly edible fats or waste fats) and microalgae oil [2]. The majority of biodiesel today is produced through homogeneous alkali-catalysed transesterification of edible vegetable oils using methanol. Such process enables a relatively short reaction time and a good product quality; however, the triglyceride source and the alcohol must be substantially anhydrous and a low free fatty acid (FFA) content of the raw material is required to avoid the production of soaps (by catalyst consumption) and low product yields [2,3].

From an economic point of view, biodiesel still has difficulties to be competitive without fiscal incentives, mostly due to the price of the raw materials and also the processing costs. The application of heterogeneous (solid) catalysts for biodiesel production might significantly alleviate the processing costs associated with homogeneous catalysis because they can be re-used, allow a better separation and quality of the final products and avoid extensive product purification steps. Such process is environmentally benign and can be applied in either batch or continuous mode [4–6].

One of the disadvantages of the heterogeneous catalysts is that they require more extreme reaction conditions (higher temperatures and reaction times are generally used) compared to the homogeneous process [7]. Solid acid catalysts (e.g. zeolites, mixed oxides, sulfated zirconia and ion exchange resins) might be very interesting for the production of biodiesel from feedstocks with high FFA contents, but still their activity is low which requires a larger amount of catalyst compared to the homogeneous process [8]. Additionally, when heterogeneous catalysts are used, a loss of catalyst is generally observed [4,8], namely through the production of soaps (alkaline catalysts) [9]. Accordingly, product purification is still required in most cases to ensure that the produced biodiesel has the required quality.

Several researchers have worked on the development of promising heterogeneous catalysts, taking into account the constraints previously referred [4,10–13]; however, the high costs associated with the catalyst preparation and biodiesel synthesis are, still, a major drawback. Previous studies evaluated the production of an heterogeneous alkaline catalyst using CaO, glycerol and methanol, which are three simple and cheap components [9,14]. The use of glycerol for catalyst preparation enables a higher efficiency of the catalyst (glycerol reduces poisoning of the active species by carbon dioxide and water) and, simultaneously, the valorization of this by- product. Such catalyst was successfully used for the transesterification of refined soybean oil, under inert atmosphere [9].

The present work studied, more deeply, glycerol enriched heterogeneous catalysts, aiming to increase their economic competiveness; for that, the following innovation goals were established:
(i) to evaluate the catalyst performance under ambient atmosphere when prepared using different glycerol concentrations and by varying selected reaction conditions; (ii) to perform biodiesel production using different triglyceride sources including soybean oil and waste frying oil, and considering key product quality requirements according to EN 14214; (iii) to access catalyst reusability;
(iv) to evaluate the possibility of using of ethanol instead of methanol for catalyst preparation; and, (v) to identify additional alter- native routes for the glycerol by-product.

2. Experimental

2.1. *Material*

The soybean oil used was from the brand “olisoja”. This oil is in agreement with the Portuguese specifications for food oil. The waste frying oil was obtained from a voluntary collection system implemented at the Faculty and consisted of waste frying oil from different domestic sources. Waste frying oil was filtered under vacuum before being used. The reagents used during synthesis and purification procedures were: methanol 99.5% (analytical grade, Fischer Scientific), nitric acid (analytical grade, Merck), calcium carbonate (analytical grade, Merck), sodium carbonate (analytical grade, Merck), glycerol (reagent grade, Aldrich), n-Heptane (analytical grade, Merck), methyl heptadecanoate (analytical standard, FLUKA), calcium standard for AAS (TraceCERT®, 1000 mg L^{-1} Ca in nitric acid, FLUKA) and CombiCoulomat frit Karl Fischer reagent for the coulometric water determination (Merck). Syringe filters (polypropylene, 25 mm diameter and with 0.2 1m of pore size) were supplied by VWR.

2.2. *Catalyst preparation*

Calcium glyceroxide was selected from the literature review and also from preliminary studies, where the evaluation of different metals for catalyst preparation was performed. The CaO was prepared by calcination of 0.1785 g of $CaCO_3$ in a tubular furnace, at 1173 K, during 4 h and under N_2 atmosphere. Once the CaO was obtained, it was placed into a small flask with 1.5 g of a protective mix (Methanol–Glycerol) with different amounts of glycerol, from 40 to 160 mg (the same procedure was performed when ethanol was used instead of methanol, using the selected glycerol amount). The catalyst was after submitted to sonication during 15 min, as described by López Granados et al. [9]. When CaO was used as catalyst alone, it was prepared from $CaCO_3$, according to the previously described procedure.

2.3. *Biodiesel production procedures*

All the procedures were performed under ambient atmosphere. The catalyst produced according to 2.2 was added to a three-necked batch reactor containing the methanol required for the reaction (methanol:oil molar ratio of 14:1) at 333 K, and mixed (magnetic stirring) with the methanol during 15 min. After, 50 g of the oil at 333 K were added to the reactor. The subsequent transesterification reaction was carried out at 333 K with vigorous stirring (stirring plate regulated to 1000 rpm) during 2–5 h, depending on the study (Fig. 1, step A). Aliquots (1.5 mL) were taken at different reaction periods. After sampling, the reaction mixture was filtered, using a syringe filter, into a 5 mL glass flask that was immediately inserted in an ice bath, to ensure the end of the reaction. Methanol was then removed from the biodiesel and the glycerol phases by distillation under vacuum, in a rotary evaporator. Each sample was treated according to EN 14103 (2003) for determination of the methyl ester content.

After the reaction, biodiesel purification was performed as follows: the catalyst was recovered by filtration (Fig. 1, step B), glycerol was separated by settling (Fig. 1, step C) and methanol was recovered using a rotary evaporator. To ensure the removal of calcium soaps, the treatment proposed by López Granados et al. [14] was performed. For that, methanol (biodiesel:methanol mass ratio of 2) containing an excess of anhydrous Na_2CO_3 (5% in respect to the biodiesel mass), at 338 K, was added to the biodiesel and stirred during 5 h (magnetic stirring plate regulated to 1200 rpm) (Fig. 1, step D). The calcium carbonate and remaining Na_2CO_3 were removed by filtration (Fig. 1, step E) and, finally, methanol was separated from biodiesel by settling. The biodiesel was after washed four times (10 min each) at 333 K, using 50 wt.% of distilled water (in respect to the biodiesel mass) and under magnetic stirring at 500 rpm. After each washing step, the mixture was decanted and the washing water was removed. Finally, biodiesel was distilled under vacuum, in a rotary evaporator, at 200 mbar and 343 K, during 1 h, to ensure the removal of remaining water.

Experiments were performed in duplicate and the results are expressed as mean values with relative percentage differences between them always less than 3% of the mean.

2.4. *Analytical methods*

The following parameters were determined: (i) oil composition, from the fatty acid methyl ester (FAME) content using gas chromatography (GC), as described by Dias et al. [5]; (ii) acid value of the oil and biodiesel, by volumetric titration according to the standards NP EN ISO 660 (2002) and EN 14104:2003; (iii) iodine value of oil/ biodiesel, determined from the esters composition according to annex B of EN 14214 (2003); (iv) water content of oil and biodiesel, by the coulometric Karl Fischer titration method (ISO 8534:2008 and EN ISO 12937) using a Karl Fischer Moisture Titrator MKC-501; and, (v) biodiesel calcium content, by atomic absorption spectrometry using a SOLAAR UNICAM AA spectrometer. For the determination of calcium, 1 g of biodiesel or 0.5 g of glycerol were dried in a hot plate at 623 K in a platinum crucible and then calcined in a furnace at 823 K during 30 min. Nitric acid (5 mL) was added to the ashes and, after. heating was performed at 473 K until the solution was reduced to 200 μL. The solution was transferred to a 50 mL volumetric flask that was completed with distilled water. Calcium cathode lamp was used at 5 mA to determine calcium concentration, with a wavelength of 422.7 nm and a slit width of 0.5 nm. To determine FAME concentration in the glycerol samples, a solvent extraction using n-heptane was performed followed by gas chromatography (GC) analysis of the extract according to EN 14103:2003.

3. Results and discussion

Different metal glyceroxides were evaluated for the transesterification of soybean oil (acid value of 0.60 mg KOH g^{-1}, iodine value of 130 cg I_2 g^{-1} and water content of 539 ppm) being prepared using CaO, CuO, ZnO or Al_2O_3, together with glycerol and methanol. However, FAME production was only detected when the calcium catalyst was used. In fact, no conversion was observed after 260 min of reaction using the other three catalysts. Therefore, the study focused on the use of the calcium glyceroxide catalyst.

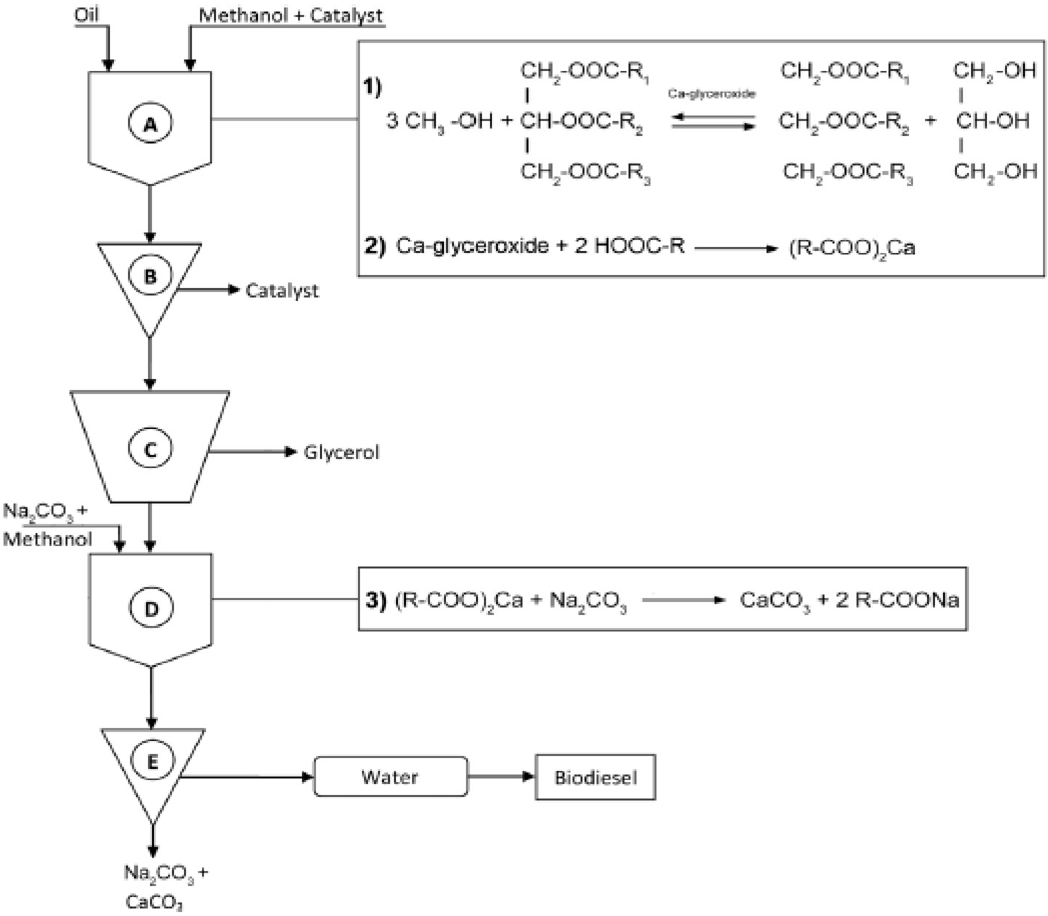

Fig. 1. Scheme of the biodiesel production, including purification steps and reactions involved. Reactions: (1) Transesterification of triglycerides using methanol and calcium glyceroxide as catalyst; (2) Saponification of fatty acids with calcium glyceroxide; (3) Reaction of calcium soap with sodium carbonate.

3.1. *Evaluation of the catalyst activity using different glycerol concentrations*

As showed by López Granados et al. [9], the glycerol amount used for catalyst preparation affects the FAME yield. In addition, it is also important to evaluate the glycerol concentration in the catalyst from the perspective of determining how much of the by-product glycerol can be recycled by this route. Apart from this, in order to have a high conversion, it was found to be crucial to have inert atmosphere during the reaction [9]. Previous work performed by the authors, on the transesterification using calcium manganese oxide as heterogeneous catalyst, showed that in fact the oxygen played an important role in catalyst deactivation [4]. In the present work, the activity of the heterogeneous catalyst was evaluated under air atmosphere (a more realistic operational condition) and using different concentrations of glycerol. In previous work [9], the amount of glycerol used ranged from 10 to 60 mg, corresponding to a variation of the mass ratio of glycerol:CaO from 0.1:1 to 0.6:1, and the best results concerning the reaction rate were observed at the higher glycerol concentrations. In such work, it was demonstrated that glycerol reacts with the surface of the calcium oxide, resulting in calcium glyceroxide species that are the ones responsible for the increase of the reaction rate (IR characterisation studies which support those findings can be found in the study). In the present work, an evaluation was performed using up to 1000 mg of glycerol, corresponding to a variation of the mass ratio of glycerol:CaO from 0.4:1 to 100:1. Fig. 2 shows the evolution of the transesterification reaction with time using soybean oil as raw material and 0.2 wt.% of the catalyst (on the basis of CaO amount) prepared using different glycerol concentrations. As expected, all the catalysts containing glycerol presented a maximum conversion always higher than that obtained using the CaO alone (0 mg of glycerol). Fig. 2 shows data only up to 180 min; the maximum FAME conversion using CaO alone was obtained after 300 min, being 92.4 wt.%. This fact indicates that the Ca-glyceroxide catalyst is less prone to deactivation by air contact (carbonation and hydration), contrary to what happens with CaO or CaO based catalysts, as observed by Dias et al. [4]. The activity of the catalyst increased as the glycerol concentration increased up to 160 mg (1.6:1 glycerol:CaO mass ratio); under such conditions, at 180 min, FAME conversion was 91.6 wt.% compared with 69.9 wt.% using CaO alone. At higher concentrations the conversion decreased. For this reason, the catalyst prepared using a mass ratio of 1.6:1 glycerol:CaO was selected as the best catalyst. This active catalyst, prepared and used at ambient atmosphere, could, therefore, recycle 2.5 times more glycerol than previously reported [9].

3.2. *Improvement of the transesterification reaction rate*

In order to improve the reaction rate, and therefore reduce the time required for the reaction, two different strategies were evaluated considering the results retained from Section 3.1. In the first methodology, instead of adding all the soybean oil to the reactor, the oil was added in aliquots of 10 g (20% of the oil amount), each 10 min, until 50 min of reaction. The objective was to have a higher catalyst concentration in the beginning of the reaction (5 times higher) to promote the faster conversion of triglycerides, by reducing the induction period [15]. Sampling was performed at each oil addition and at different intervals of time up to 260 min of reaction, as shown in Fig. 3a. The rate of the reaction was not influenced by the addition of the oil step by step; on the contrary, the FAME conversion was maintained in a mean of around 35 wt.%

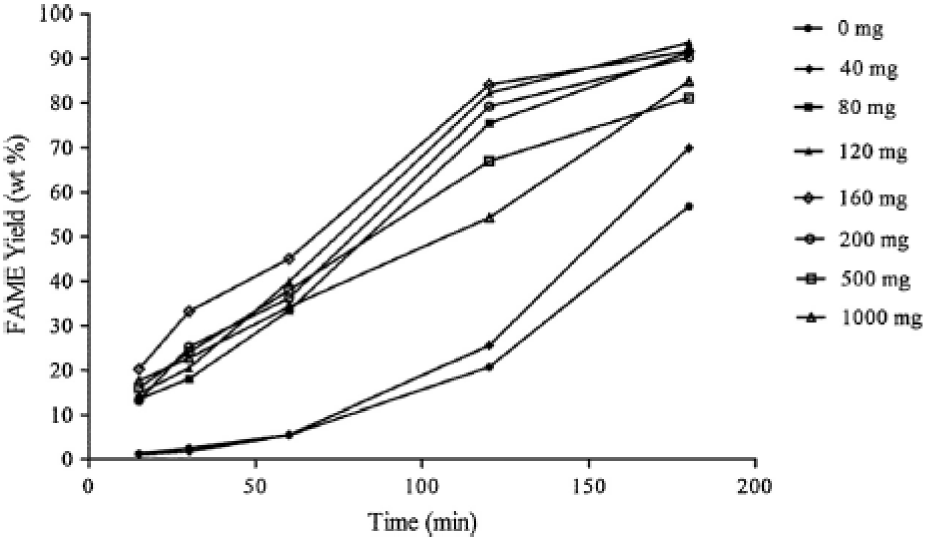

Fig. 2. Evolution of FAME production with time when Ca-glyceroxide was produced with different amounts of glycerol. Reaction conditions: 50 g of soybean oil; 0.2 wt.% of catalyst (based on CaO amount), methanol:oil molar ratio of 14:1, 333 K and 1000 rpm.

during the first 50 min. After that time, the reaction rate increased and 94 wt.% of FAME was obtained after 260 min. A significant increase of FAME yield occurred from 70 to 80 min. One explanation for this finding might be that the produced FAME, mono and diglycerides present at the same time act as an emulsifier, reducing the mass transfer limitations between methanol and oil, therefore causing the increase of the reaction rate [16].

Although good results were obtained, this procedure was not competitive with the one previously performed (Fig. 2). In the second methodology, the reaction was carried out in two steps, of 60 min each, and the separation of the glycerol was performed after the first step to shift the reaction equilibrium towards the products [17]. In order to do that, after the first step the catalyst was filtered, glycerol was removed by settling and the methanol in excess was recovered. The organic (ester) phase was then placed again in the reactor for the second step, under the same conditions used for the first one. Samples were taken in the middle and in the end of each step to evaluate FAME yield. Fig. 3b shows that FAME conversion after the first step was, as expected, similar to the one obtained previously in the one step process (44.9 wt.%, Fig. 2). In the second step, the conversion at 30 and 60 min was 71.7 wt.% and 87.0 wt.%, respectively. Although an increase was observed in the second step, the differences between what was obtained in the one step process (Fig. 2) do not justify changing the process.

3.3. *Evaluation of the influence of catalyst concentration on biodiesel yield*

The alternatives previously studied did not show significant improvement, compared with the initially studied process (Section 3.1) in order to make this catalyst more competitive compared to the homogeneous alkali catalyst, since the reaction time was still high (180 min) and also a high methanol:oil molar ratio was required (14:1). For that reason, the influence of catalyst concentration on product conversion was also studied.

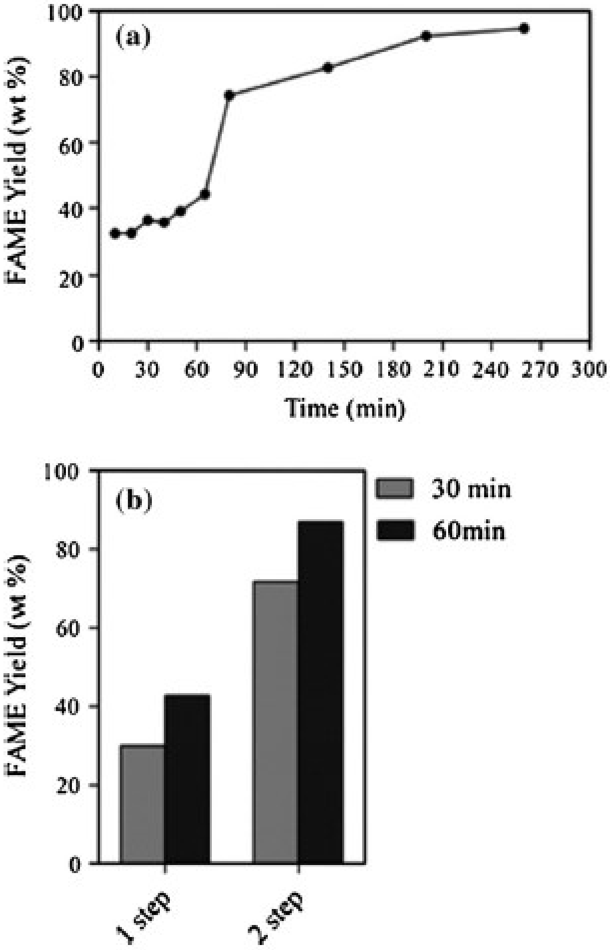

Fig. 3. Strategies to improve the reaction rate. (a) Soybean oil added in aliquots of 10 g, each 10 min until 50 min; (b) Reaction performed in two steps of 60 min and samples taken in the middle and end of each step. Reaction conditions: 0.2 wt.% of catalyst (based on CaO amount), methanol:oil molar ratio of 14:1, 333 K and 1000 rpm.

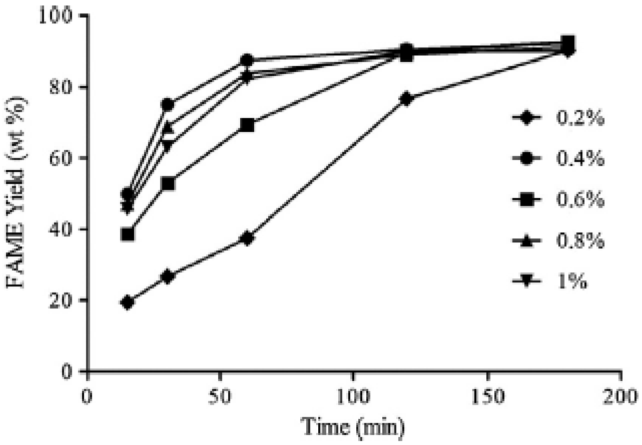

Fig. 4. Influence of the catalyst concentration in methyl ester yield. Reaction conditions: 50 g of oil, methanol:oil molar ratio of 14:1, 333 K and 1000 rpm.

The results, presented in Fig. 4, show that the transesterification reaction using soybean oil as raw material was faster when 0.4 wt.% catalyst was used, compared to the 0.2 wt.% concentration previously studied.

A further increase of the catalyst concentration does not have a positive effect on the rate of the reaction. Using 0.4 wt.% of catalyst, the reaction time could be reduced to 120 min. FAME yield was 90.4 wt.% and a calcium concentration of 299 ppm was observed in the product, meaning that the product still required purification. The calcium concentration was similar to the one found in the study by López Granados et al. [9] (approx. 300 ppm), meaning that the same degree of soap production occurred. However, the soy- bean oil used in the present study presented significantly higher free fatty acid content (around 6 times). This fact might indicate that some conversion of FFA to FAME occurred in this process. Table 1 summarizes the key quality parameters of the purified bio- diesel under the selected reaction conditions. It can be observed that all values are in agreement with the EN 14214 quality standard.

3.4. *Evaluation of the influence of methanol:oil molar ratio on biodiesel yield*

The mechanism by which alkali catalysts act during transesterification is relatively well known. The methoxide ion (CH_3O^-) generated by contact of methanol and the basic sites of the catalyst attacks the carbonyl group of tri, di or monoglycerides leading to the production of methyl esters and di and monoglyceroxides anions. The glyceroxide anions cannot be dissolved in the liquid phase but stay near to the positive counter ion on the catalyst sur- face, which causes poisoning of its active sites [18]. In addition, the reaction occurs in three phases: catalyst/alcohol/triglyceride, which causes mass transfer difficulties. For these reasons, the heterogeneous basic catalysts are less active than the homogeneous ones and usually it is necessary to conduct the reaction at a higher temperature, pressure and/or methanol to oil molar ratios to achieve high conversions [18]. In fact, usually at least 4 times the stoichiometric amount of methanol is used [4], whereas in homogeneous catalysis the reaction is conventionally performed using the double of the stoichiometric amount (6:1) [19]. Aiming to evaluate the effect of this parameter on biodiesel yield, the reduction of the methanol:oil molar ratio from 14:1 to 7:1 was studied and Fig. 5 shows the evolution of the transesterification reaction with time at both ratios. During the progress of the reaction, a decrease of approximately 5% was observed when using a 7:1 methanol:oil molar ratio, compared to when a 14:1 ratio was used; however, after 120 min of reaction, only a 2% difference was observed. Such result is very promising as it allows the reduction of processing costs and also shows that it is possible to use this catalyst in conditions close to the ones used in homogeneous catalysis.

3.5. *Reuse of the catalyst*

One of the most important advantages of the heterogeneous catalysts, compared to the homogeneous ones, is that they can be re-used. Therefore, it is very important to evaluate how many times the catalyst can be reused, under the selected reaction conditions. Because there was some catalyst loss (mostly as soap, as it will be further explained), in the experiments preformed to evaluate the catalyst reuse, 1% of catalyst concentration was used (amount conventionally used in homogeneous catalysis), to ensure that enough catalyst would exist to perform all active cycles. It should be emphasised that the catalyst activity during the transesterification reaction was similar using 0.4 or 1 wt.% of catalyst (Fig. 4). The catalyst was recovered after each run, by filtering, and used in a new catalytic test; the results showed that the catalyst could be reused during four consecutive cycles without loss of activity (Fig. 6). In the fifth cycle, the FAME conversion decreased until 65.5 wt.% The results demonstrate the advantage if using this catalyst, being very good and consistent with the best results of the literature, where catalyst could be reused during three or four cycles maximum [20,21]. The decrease of the catalyst activity might be explained by the production of calcium soaps taking into account that a 10% loss as calcium soap to the biodiesel and the glycerol phase was determined; such values agree with other studies [20,21].

Table 1
Biodiesel quality using the selected catalyst and virgin soybean oil and waste frying oil as raw materials.

Property	Result		EN 14214
	Soybean oil	Waste frying oil	
Acid value (mg KOH g^{-1})	0.33	0.71	Max. 0.50
FAME content (wt.%)	97.0	95.5	Min. 96.5
Ca^{2+} (ppm)	<3	<5	Max. 5
Water content (ppm)	125	213	Max. 500

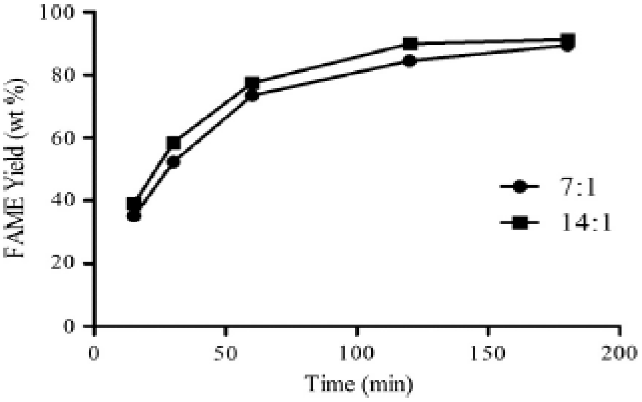

Fig. 5. Influence of methanol:oil molar ratio in methyl ester yield. Reaction conditions: 50 g of soybean oil; 0.4 wt.% catalyst (based on CaO amount), 333 K and 1000 rpm.

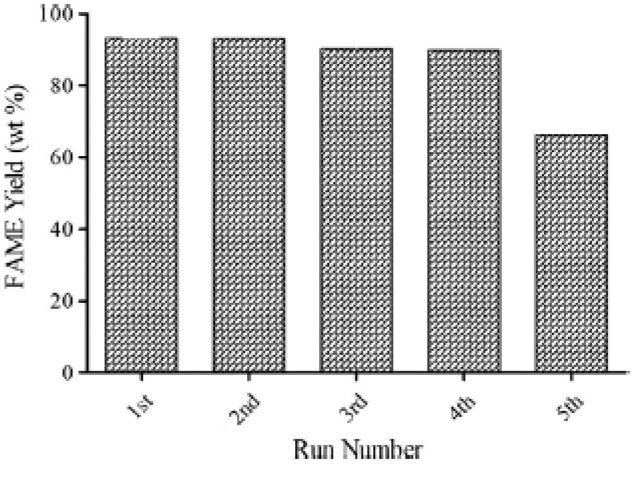

Fig. 6. Catalyst reuse. FAME yield (wt.%) obtained after successive runs. Reaction conditions: 1 wt.% Catalyst (based on CaO amount), 333 K, methanol:oil molar ratio of 14:1, 1000 rpm and 120 min of reaction.

3.6. *Use of ethanol instead of methanol for catalyst preparation*

In order to improve the safety and reduce the environmental impacts related to catalyst preparation and storage, the use of ethanol instead of methanol was studied. With that purpose, the catalyst was prepared in the same way, by replacing the methanol by ethanol, and after the catalyst was used in the transesterification reaction under the best conditions previously selected. The results presented in Fig. 7 favour the use of ethanol, since during the progress of the reaction the differences in FAME conversion were small; in fact, after 180 min, an 88.19 wt.% conversion was observed using the catalyst prepared with ethanol compared to a 91.60 wt.% conversion using methanol.

3.7. *Evaluation of alternatives for the glycerol by-product*

The sections previously presented aimed at evaluating the best conditions to produce and efficiently apply an heterogeneous glycerol enriched catalyst for biodiesel production using sunflower oil as raw material. An additional concern towards improving the economic competitiveness of biodiesel production is the management of the glycerol by-product.

In fact, due to the great amounts of glycerol currently produced by the biodiesel industry, such a by-product, initially considered an advantage of the process, currently does not have efficient management alternatives [22]. Its application for catalyst preparation may be very relevant and interesting but, in this alternative, only some of the glycerol will be used. In addition, in order to be used with other purposes, the glycerol requires a costly purification and it is extremely relevant to find alternatives that can enable its use as directly as possible. The potential of using glycerol as animal feed has been identified. Several authors indicate that glycerol is a suitable supplement in cow food and it has been shown that glycerol can be included in an amount of at least 15% of the dry matter in diets for lactating dairy cattle, without having an adverse effect on milk production or milk composition [23–25]. In addition, the digestibility of calcium soaps has been demonstrated, when used as supplement in animal food; the presence of these salts enhances the digestibility of all dietary components and also allows an increased energy for lactation [26,27]. The present study showed that the glycerol by-product of the process, using soybean oil as raw material, was mostly rich in calcium soaps (4683 ppm of Ca^{2+}); no FAME was detected. The concentrations found indicate that, using this raw material, 94% of the leached catalyst was in the glycerol phase, in the form of calcium soaps. This shows that if an industrial process is implemented, after the removal of the excess alcohol, such a by-product might be directly applied, presenting a much higher added-value (in this case the catalyst loss adds value to glycerol), compared to the one obtained from an homogeneous process or other heterogeneous processes [28]. This fact shows an additional advantage of using this catalyst.

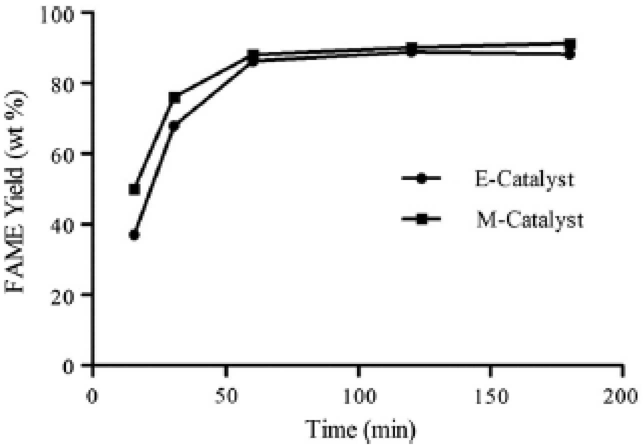

Fig. 7. Progress of the reaction using ethanol or methanol for catalyst preparation. Reaction conditions: 50 g of soybean oil; 0.4 wt.% catalyst (based on CaO amount), 333 K and 1000 rpm.

3.8. Biodiesel production from waste frying oil

In the previous sections, the evaluation of the heterogeneous process was conducted considering the use of a refined oil; how- ever, the use of wastes as raw material presents very high interest considering the reduction of costs (up to 80%) and, especially, the implementation of more environment-friendly processes, since waste oils are responsible for high environmental impacts [29]. Constraints regarding the future sustainability of some sources of waste oil, such as waste frying oils (lower availability) should how- ever be taken into account [30]. In addition, variations in the waste oil/fat characteristics will affect product quality, both in homogeneous and heterogeneous process (less susceptible), reason why it is important to evaluate each source separately and consider, if necessary, the use of blends [5,30].

In this section, results are presented on the evaluation of the application of the developed catalyst for biodiesel production from wastes. Experiments were conducted using waste frying oil (acid value of 0.77 mg KOH g^{-1}, iodine value of 127 cg I_2 g^{-1} and water content of 652 ppm) and the selected catalyst, under the best conditions previously established.

After the reaction, the FAME conversion was 89.0% and the calcium concentration was 628 ppm; therefore, the product required further purification (note that the calcium concentration in this case was roughly the double compared to the one using virgin oil). Biodiesel was purified in the same way as for the virgin oil and the final quality of the product was assessed, being also presented in Table 1. In fact, the major difference compared to the biodiesel obtained from the virgin oil relates to the calcium concentration and this should be due to both the water content and the acid value of the waste oil; however, the product presented good quality since the difference found to achieve the minimum FAME content was around 1% (within an acceptable margin of error). Since calcium concentrations differed, the glycerol quality is expected to be different that obtained using virgin oil; therefore, future studies should be conducted to evaluate the potential of this by-product.

4. Conclusion

The most active glycerol enriched catalyst was produced using CaO, glycerol and methanol at a mass ratio of 1:1.6:13.4, respectively. The advantages of using such catalyst are that it could be used under air atmosphere, in the presence of free fatty acids, re- used four times without loss of activity and, prepared using ethanol instead of methanol, with differences less than 4% in product conversion.

In addition, using virgin vegetable oil or waste frying oil as raw materials, it was possible to produce good biodiesel by performing the transesterification using the developed glycerol enriched catalyst, at promising conditions compared to the ones used for homogeneous catalysis (0.4 wt.% catalyst, 7:1 methanol to oil molar ratio, 2 h, 333 K).

The catalyst loss into the glycerol phase occurred as calcium soaps and such fact might be an important advantage to apply this by-product for the enrichment of animal diets, enabling a two-way recycling of the by-product glycerol.

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